

REMARKS

Claims 1-8 are pending.

Claims 7 and 8 have been withdrawn.

Claims 2-5 are currently amended.

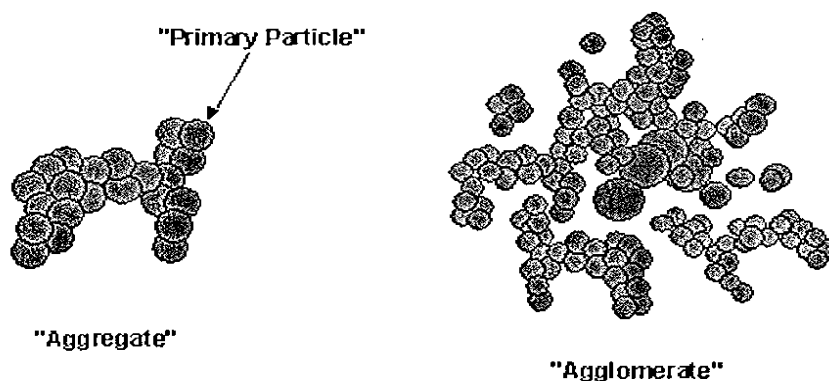
The rejection of Claims 1-6 under 35 U.S.C. § 102 in view of either U.S. Patent 6,534,232 to Matsuda et al. (102(e)) and/or the Japanese priority application publication JP 2001-027829 of Matsuda et al. (102(b)) is traversed. It is believed that the claimed invention is patentably distinct from the cited prior art, and it is requested that the Examiner reconsider the rejections in view of the following comments.

In short, there are two salient differences between Applicants' claimed invention and Matsuda's disclosures. Firstly, Applicants' average core particle size is different from Matsuda's average core particle size. Additionally, Applicants have determined that the carbon black number average diameter (CBDN) within the coating layer is dependent upon the conditions used to prepare either the coating liquid or a given carrier material (see below). Matsuda does not specify the conditions used to prepare the coating liquid. Therefore, the size of the carbon black particles in Matsuda's examples cannot be the same as that described in Applicants Specification, and, thus, Matsuda cannot anticipate Applicants' claimed invention. The following text provides further clarification and support for these assertions.

The Examiner has noted that Matsuda's Carrier D (col. 11, ll. 8-63) appears to be identical to Applicants' Carrier I (see Example 1 pages 18-19), and he supported this notation by indicating that the specific resistance of the two carriers is identical. Applicants direct the Examiner's attention to Matsuda's disclosure of the "SM-400" carrier core material (col. 10, l. 4), where it states that the average particle diameter of "SM-400" is 44 μm . On the other

hand, Applicants' carrier core material has an average particle size of 48 μm for Carrier (I) (p. 19, ll. 25-26) and 50 μm for Carrier (II) (p. 24, ll. 25-26). Therefore, Applicants' carrier core particles of Carrier (I) are larger than Matsuda's carrier core particles of Carrier D. Since the two differently sized carriers share a coating layer with the same starting chemical composition, there must be something different between the two species since they have the same specific resistance. This difference resides in the carbon black number average diameter (CBDN) within the resin layer. The question that arises is how can the size of the carbon black particles vary? In order to answer this question, and consequently address all of the outstanding rejections, it is informative to discuss the structural forms of carbon black. Applicants direct the Examiner's attention to Figure 1,¹ and a photocopy of a selected portion of Kirk-Othmer's "Carbon (Carbon Black)," both of which will serve as aids for the following discussion.

Figure 1. Carbon black particles.



¹ See attached publically available reference material from Cabot Corp. – Special Blacks Division

As noted in Kirk-Othmer (see attachment, p. 1041), and illustrated in Figure 1, there are three different "particles," i.e., particles (primary particles or nodules), aggregates, and agglomerates, within a sample of carbon black. Primary particles, of approximately the same size, fuse together during the production process to form aggregates of widely differing sizes. Interactions between aggregates give rise to larger assemblies, which are referred to as agglomerates. It can be inferred from inspection of Figure 1, and the attachment (Kirk-Othmer, p. 1043, Table 1), that the size of the particles obeys the following trend:

primary particles < aggregates < agglomerates.

In the case where carbon black is dispersed within a hot polymer melt, the agglomerates experience shear forces that tend to break-apart the agglomerated species. When the shear forces acting on the agglomerates exceed the interactive forces between associated aggregates, the agglomerates will dissociate to liberate the smaller aggregate particles. As noted in Kirk-Othmer, "high shear energy, usually ultrasonic, and enough time are employed...to break down microagglomerates" to aggregates (see Attachment, p. 1045, ll. 10-12). In the hot polymer melt, the extent of dissociation of the agglomerates into the aggregates is dependent upon the shear forces that are exerted upon the agglomerates. Additionally, if the shear forces are great enough, "the aggregates themselves undergo fracture forming smaller aggregates" (Kirk-Othmer, p. 1045, ll. 12-14). In view of the relationship between the primary particles, aggregates, and agglomerates, a closer examination of Applicants' claimed invention is in order.

Applicants have determined that the size of the carbon black particles, i.e., the collective whole of fractured aggregates, aggregates, and agglomerates in the coating layer,

can be controlled at two separate stages during the production of the carrier particles: (1) when the coating liquid is prepared by dispersing the individual components in a homomixer and (2) when the coating liquid is sprayed onto the core particles. For convenience, Applicants present Table 1, which tabulates comparative data for the carriers described in the Specification.

Table 1. Comparative Data for Carriers (I) – (IV)

Property or Condition	Carrier (I) ^a	Carrier (II) ^b	Carrier (III) ^c	Carrier (IV) ^d
Core Particle Size, μm	48	50	48	48
Coating Liquid	I ^e	I ^e	I ^e	II ^f
Dispersion Conditions				
Mixing Temp., $^{\circ}\text{C}$	35-40	35-40	35-40	35-40
Mixing Time, min	20	20	20	5
Coating Conditions				
Device Temp., $^{\circ}\text{C}$	70	70	100	70
Heating Conditions	300 $^{\circ}\text{C}$, 2hr	300 $^{\circ}\text{C}$, 2hr	300 $^{\circ}\text{C}$, 2hr	300 $^{\circ}\text{C}$, 2hr
CBDN, nm	40	40	7	160
Specific Resistance, $\Omega\cdot\text{cm}$	2.0×10^{13}	1.5×10^{13}	7.9×10^{15}	5.0×10^9
Image Density	1.41	1.45	1.19	1.50
Reproducibility of Fine Line Image	4	5	4	3
Others	No problem	No problem	Edge Effects	White Spots

^ap.19, ll. 10-29. ^bp.24, l. 20 – p. 25, l. 5. ^cp. 25, l. 7 – p. 26, l. 7. ^dp. 27, ll. 5-19. ^ep. 18, l. 30 – p. 19, l. 9. ^fp. 26, l. 21 – p. 27, l. 4.

Carriers (I) and (II) are described in examples 1 and 2, respectively. While Carriers (III) and (IV) are described in comparative examples 3 and 4, respectively. For quick reference, footnotes are provided that identify the page and line numbers of the various terms that are located in the Specification. Referring to Table 1, it can be seen that the core particle size for Carriers (I), (III), and (IV) are the same (48 μm), while the core particle size for Carrier (II) is slightly larger (50 μm). There are two types of coating liquid, designated

Coating Liquid I and II, that are used to coat the carrier core particles. They comprise the same starting chemical components in the same proportion, and differ only in the amount of time required to disperse said chemical components. All of the carrier core particles are coated in a similar manner, i.e., they are placed on a rotary bottom disc of a fluidized bed of a coating device. The temperature of the coating device is set to 70°C for Carriers (I), (II), and (IV), and 100°C for Carrier (III). The CBDN of Carriers (I) and (II) are the same (40 nm), but the CBDN for Carrier (III) (7 nm) and Carrier (IV) (160 nm) are both different. The CBDN measurement was accomplished using electron microscopy (see Specification p. 15, l. 35 through p. 16, l. 12). Inspection of the Table shows that an increase of 2 μm of the average core particle size (*cf.* Carriers (I) and (II)) results in a 25% reduction in the specific resistance value.

As noted above, there are two ways in which the carbon black particle size can be altered. One way is to reduce the dispersion time. Inspection of the "coating liquid dispersion conditions" shows that reducing the mixing time from 20 min (Carrier (I)) to 5 min (Carrier (IV)) gives rise to four-fold increase in the carbon black particle size (i.e., 40 nm vs. 160 nm). Referring back to the discussion of agglomerate formation from aggregates, this makes sense when one considers that carbon black samples principally contain agglomerations of carbon black aggregates. Understanding that the mere act of dispersing (or mixing) the chemical components together gives rise to shear forces that serve to disrupt the aggregate-aggregate interactions, and, thus, reduces the extent of agglomeration within a given sample. A reduction in the number of agglomerates gives rise to a smaller carbon black particle size within the coating layer. Conversely, a longer dispersing time subjects the carbon black agglomerates to the shear forces for a greater amount of time, and thus, leads to an overall reduction in the size of the particles.

Additionally, carbon black particle size may be altered by varying the temperature of the coating device. Inspection of the table shows that the coating device temperature for Carrier (I) is 70°C (p. 19, lines 19-20), while the coating device temperature for Carrier (III) is 100°C (p. 26, ll. 1-2). This thirty degree temperature difference results in a 5.7-fold reduction in the average carbon black size of Carrier (III) (7 nm) with respect to Carrier (I) (40 nm).

As noted above, the specific resistance of the carrier particle is inversely proportional to the size of the carbon black particle within the coating layer of the carrier particle. For example, when the particle size is too small, i.e., $< 0.01 \mu\text{m}$, the specific resistance is unacceptably high ($7.9 \times 10^{15} \Omega\cdot\text{cm}$; cf. Carrier (III)). Conversely, when the particle size is too large, i.e., $> 0.1 \mu\text{m}$, the specific resistance is too small ($5.0 \times 10^9 \Omega\cdot\text{cm}$; cf. Carrier (IV)). The data in the table reveals that a higher quality electroconductive image is obtained with a developer that comprises a carrier, which comprises carbon black particles impregnated in a coating layer whose number average particle diameter is of from $0.01 - 0.1 \mu\text{m}$, which is the decisive limitation of Applicants' claimed invention.

In regard to the rejection of Claims 1-6, there are several distinguishing points to note concerning the disclosures of Matsuda. Matsuda does not disclose that the electroconductive image can be influenced by controlling the size of the impregnated carbon black particles within the coating layer of the carrier particles. Moreover, Matsuda does not disclose that the size of the carbon black particles can be altered depending upon the manner in which the coating liquid and the carrier particles are prepared. In fact, Matsuda is silent with respect to the temperature and mixing time conditions used for the preparation of the coating liquid, and does not measure the size of the carbon black particles within the coating layer. Hence, it is

impossible to know the carbon black particle size within Matsuda's carrier particle. Additionally, Matsuda uses differently sized carrier core particles requires. Therefore Matsuda's two disclosures cannot anticipate Applicants' claimed invention, as they neither disclose nor inherently possess Applicants' claimed limitation of having carbon particles having a number average particle diameter of 0.01-0.1 μm . Applicants kindly request that the Examiner withdraw this rejection.

In a similar vein, the rejection of Claims 1 and 6 under 35 U.S.C. § 102(b) in view of Yoshino et al. (US 5,849,448) is traversed.

Yoshino employs Cabot's Regal 330 (R330) with a particle size of 25 nm (Example 1), and Vulcan XC72 with a particle size of 30 nm (Example 4), as an electroconductive particle within the resin layer. Particle sizes of 25 and 30 nm afford aggregate sizes of approximately 93 and 103 nm, respectively (see Kirk-Othmer, Table 1, p. 1043), and, thus, give rise to agglomerates that are much larger. Since Yoshino does not report the size of the particles within the resin layer, it is impossible to say exactly what average carbon black particle size is present in these carrier particles. Unless Yoshino employed techniques that produced shear forces great enough to fracture the aggregates, it is reasonable to assume that Yoshino's average particle diameter is greater than 100 nm (0.1 μm). With this in mind, Applicants request that the Examiner withdraw this rejection.

In a like manner, the rejection of Claims 1-6 under 35 U.S.C. 103(a) over Yoshino in view of Shintani et al. (US 5,204,204) and the teachings of Diamond in "Handbook of Imaging Systems" is traversed. As noted above, Yoshino lacks a critical limitation, and simply put, the additional references do not supply what is lacking in Yoshino's disclosure.

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Reply to Office Action of May 27, 2003

Since the combined references fails to teach all of the claim limitations, Applicants request that the Examiner withdraw this rejection.

RESPONSE TO RESTRICTION

Restriction to one of the following inventions has been required under 35 U.S.C.

§ 121:

- I. Claims 1-6, drawn to a carrier and developer, classified in class 430, subclass 111.1
- II. Claim 7, drawn to a method, classified in class 430, subclass 125.
- III. Claim 8, drawn to an image forming apparatus, classified in class 399, subclass 359.

Applicants have elected with traverse Group I, i.e., Claims 1-6.

Restriction is only proper if the Claims of the restricted groups are either independent or patentably distinct (MPEP § 803). The burden of proof is on the Examiner to provide reasons and/or examples, to support any conclusion in regard to patentable distinctness (MPEP § 803). Applicants respectfully traverse the Restriction Requirement on the ground that the Examiner has not carried the burden of providing any material reasons and/or examples to support the conclusion that the claims of the restricted groups are patentably distinct.

If the Restriction Requirement is not withdrawn, it is noted that Applicants have elected Claims to a Group I. Should the Examiner determine that the elected claims are allowable, then it is respectfully requested that the Examiner permit rejoinder of the process and apparatus claims that include all the limitations of the allowed product claim. If the search and examination of an entire application can be made without serious burden, the Examiner must examine it on the merits, even though it includes Claims to distinct or independent inventions.

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Applicants file concurrently herewith copies of the Information Disclosure Statement (IDS), PTO Form 1449, and complete copies of all U.S. Patents cited therein, and the List of Related Cases filed on October 30, 2002, with a copy of the date-stamped filing receipt. Applicants kindly request that the Examiner consider U.S. Patent 6,406,826, which was cited within the IDS filed on October 30, 2002.

No new matter is believed to have been added upon entry of the amendment. Applicants believe that the claims are in a condition for allowance.

Respectfully submitted,

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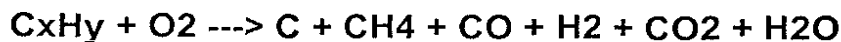
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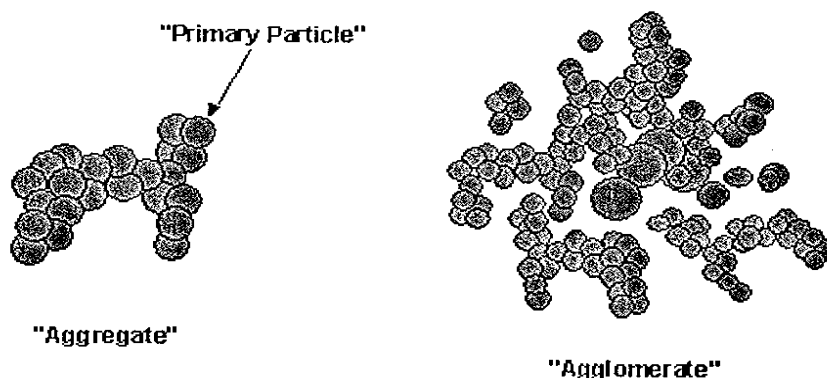
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Carbon Black: What Is It and How Is It Made?

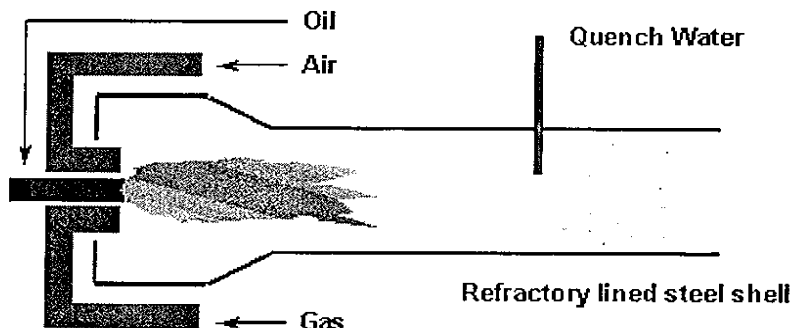
Carbon black is essentially an elemental carbon in a form different from diamond, cokes, charcoal and graphite. It consists of spherical like particles and is manufactured by the incomplete combustion of a heavy aromatic feedstock in a hot flame of (preheated) air and natural gas:



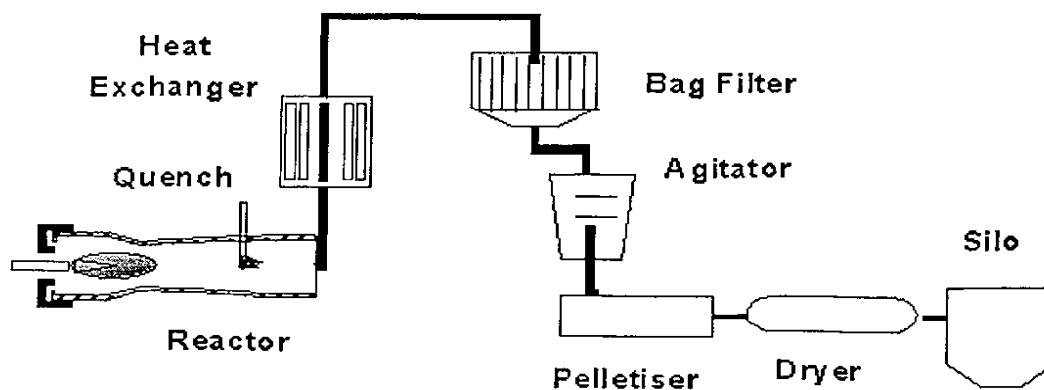
The primary units of carbon black are aggregates, which are formed when particles collide and fuse together in the combustion zone of the reactor. Several of those aggregates may be held together by weak forces to form agglomerates. These agglomerates will break down during mixing into rubber, so the aggregates are the smallest ultimate dispersible unit of carbon black. The difference between primary particle, aggregate and agglomerate is presented below:



All Cabot carbon blacks are produced using the Oil Furnace process, in which feedstock is injected into a hot gas flame zone in an enclosed reactor. A simplified schematic picture of the Oil Furnace reactor is shown in the next figure:



A broad range of carbon black types can be made by controlled manipulation of the reactor conditions. The carbon black formation reaction in the furnace is controlled by steam or water spray. The carbon black particles produced are conveyed through the reactor, cooled and continuously collected via filters. A simplified schematic picture of the carbon black overall process is shown below:



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CABOT

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CARBON BLACKS

FOR SPECIALTY APPLICATIONS



PLASTICS

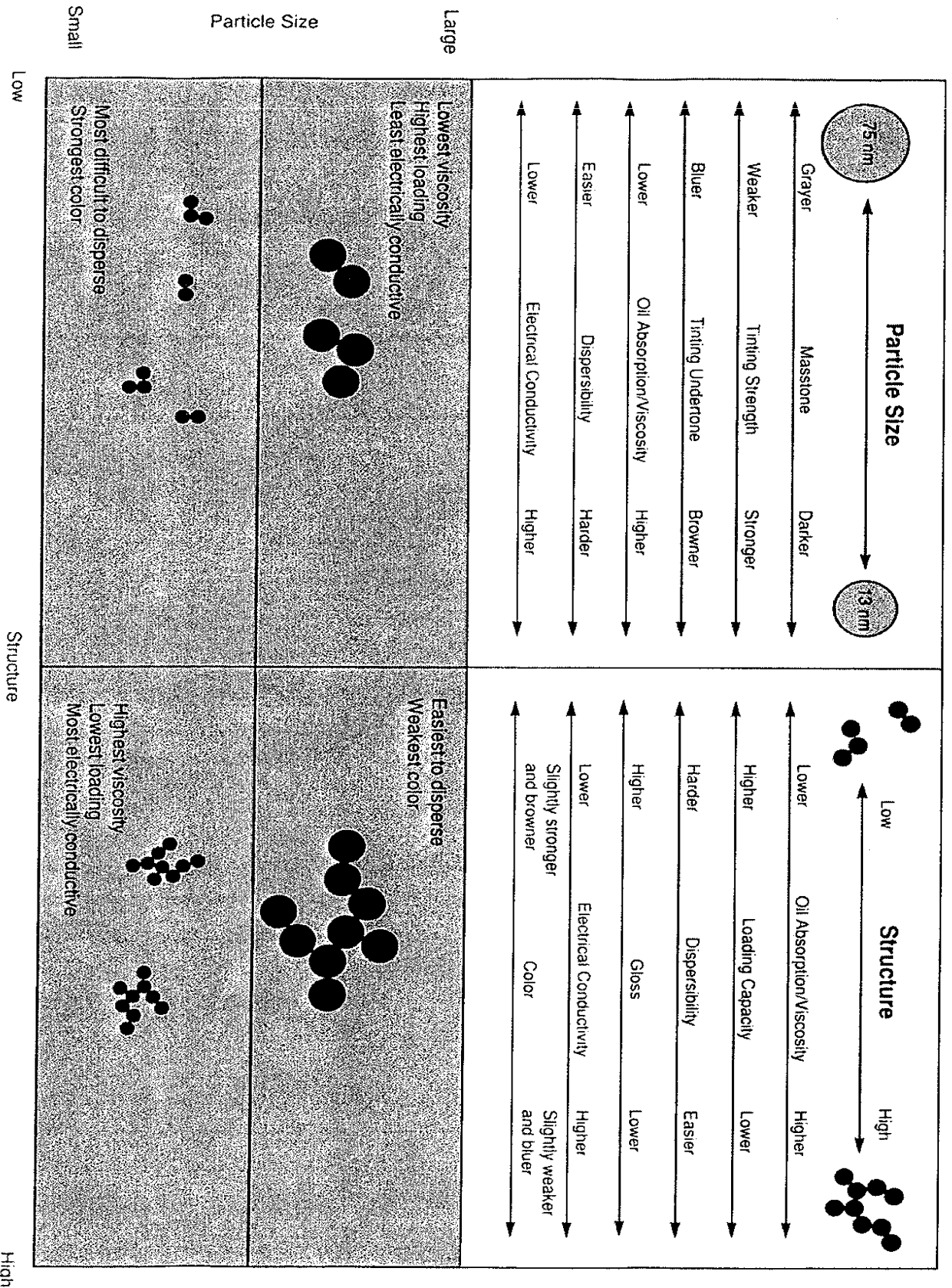


INKS



COATINGS

Typical performance properties of Carbon Blacks may be represented as follows:



	FLUFFY	PELLETS	Nitrogen Surface Area N ₂ SA (m ² /gram)	DBP Oil Absorption (cc/100 grams)		Particle Size (nm)	Tinting Strength ASTM (%)	Density (lbs./ft ³)		DESCRIPTION
				Fluffy	Pellets			Fluffy	Pellets	
HIGH COLOR	MONARCH® 1400*	BLACK PEARLS® 1400*	560	90	82	13	114	21	27	COATINGS: Superior blacks with good viscosity, stability in solvent and excellent dispersibility.
	MONARCH 1300*	BLACK PEARLS 1300*	560	100	91	13	114	20	25	
	MONARCH 1100*	BLACK PEARLS 1100*	240	65	50	14	146	15	29	PLASTICS: High fineness with neutral pH.
	MONARCH 1000*	BLACK PEARLS 1000*	343	110	105	16	146	13	24	COATINGS, TONERS: High fineness and charging for electrostatic toners.
MEDIUM COLOR	MONARCH 900	BLACK PEARLS 900	230	70	64	15	151	14	27	PLASTICS, COATINGS: Medium-high jetness.
	MONARCH 880	BLACK PEARLS 880	220	112	105	16	153	8	21	PLASTICS, COATINGS: Medium jetness. BP800 and BP900 similar in jetness. BP800 easier to disperse. While BP600 provides greater jetness, BP700 is easier to disperse.
	MONARCH 800	BLACK PEARLS 800	210	74	68	17	148	15	27	
	MONARCH 700	BLACK PEARLS 700	200	122	117	18	148	9	19	
CONDUCTIVE	—	BLACK PEARLS 2000	1500	—	330	12	164	—	9	PLASTICS, COATINGS: High conductivity at low loadings for excellent retention of physical properties.
	VULCAN® XC72R	VULCAN XC72	254	192	174	30	87	6	16	PLASTICS, COATINGS: An industry standard for conductive and anti-static applications.
	—	VULCAN PA90	140	—	116	17	92	—	22	PLASTICS: Easier processing conductive black.
REGULAR COLOR	—	VULCAN 9A32	140	—	114	19	120	—	22	PLASTICS: Excellent UV protection and good jetness — an industry standard for polyethylene cable jacketing.
	MOGUL® L*	BLACK PEARLS L*	138	62	60	24	130	15	31	INKS, COATINGS, PLASTICS, TONERS: Excellent flow, gloss and strength in high quality inks. Very good dispersion and stability in coatings. Good jetness and charging for electrostatic toners. Least conductive carbon black.
	REGAL® 660R	REGAL 660	112	65	60	24	137	15	30	PLASTICS, INKS, COATINGS: High tinting strength and low viscosity. A black widely used in fiber applications.
	—	BLACK PEARLS 570	110	—	114	24	114	—	22	PLASTICS, COATINGS: General purpose carbon blacks.
	—	BLACK PEARLS 520	110	—	92	24	117	—	24	
	REGAL 400R*	REGAL 400*	96	71	69	25	115	14	30	INKS, COATINGS: Excellent flow, dispersion and gloss in inks. Good stability and tinting strength in coatings.
	REGAL 330R	REGAL 330	94	65	70	25	122	16	28	INKS, COATINGS, PLASTICS, PAPER: Good tinting strength, jetness and dispersion.
	REGAL 300R	—	80	85	—	27	113	12	—	
	—	BLACK PEARLS 490	87	—	124	25	102	—	21	INKS: Good dispersion, blue tone and stability in liquid inks.
	—	BLACK PEARLS 480	85	—	120	29	113	—	21	PLASTICS: High structure blacks offering good tinting strength with blue tone.
	—	BLACK PEARLS 470	85	—	114	29	116	—	22	
	—	BLACK PEARLS 460	84	—	102	29	100	—	23	
	—	BLACK PEARLS 450	81	—	72	27	110	—	29	INKS, PLASTICS, PAPER: General purpose black. Unique pellet properties of BP450 provide dispersion advantage over REGAL.
	—	BLACK PEARLS 430	80	—	72	27	109	—	29	INKS: Good dispersion, blue tone and stability in liquid inks.
	—	BLACK PEARLS 420	73	—	120	26	101	—	22	
	—	BLACK PEARLS 410	73	—	124	27	97	—	21	
	REGAL 350R	REGAL 350	58	46	46	48	90	19	32	INKS: Low viscosity allowing high loading in ink bases. Excellent gloss and strong blue tone. REGAL 350 offers bluer tone and easier dispersion than REGAL 250.
	REGAL 250R	REGAL 250	55	46	46	34	101	19	32	INKS: General purpose carbon black for inks offering balance of good dispersion and blue tone.
	REGAL 99R	REGAL 99I	46	65	63	38	97	16	28	
	—	ELFTEX® PELLETS 115^	66	—	118	27	92	—	17	INKS: Oil bound pellet with outstanding dispersion in letterpress and web offset newsinks. Not recommended for low rub systems.
	ELFTEX 8	—	85	99	—	27	92	11	—	INKS, COATINGS, SEALANTS: Excellent dispersion and stability with medium strength and blue undertone.
	ELFTEX 5	—	80	118	—	27	94	8	—	
UTILITY GRADES	ELFTEX 12	—	43	95	—	37	80	10	—	INKS, COATINGS, SEALANTS: Excellent dispersion and stability with medium strength and blue undertone. Recommended as a lampblack replacement.
	MONARCH 280	BLACK PEARLS 280	42	137	121	45	60	9	22	PLASTICS, COATINGS, INKS: Easy dispersing blacks yielding smooth compound surfaces. Blue tone for lampblack replacement.
	—	BLACK PEARLS 170	35	—	122	50	60	—	22	
	—	BLACK PEARLS 160	35	—	90	50	60	—	26	PLASTICS, COATINGS, INKS: Large particle size, easy to disperse blacks allowing high loadings for most systems. Provides very blue tint tone.
	—	BLACK PEARLS 130	25	—	70	75	54	—	31	
	MONARCH 120	BLACK PEARLS 120	25	72	64	75	58	15	32	

* SURFACE TREATED GRADES (see pH below)

PERCENT VOLATILE CONTENT:

MONARCH/BLACK PEARLS 1400/1300 - 9.5, MONARCH/BLACK PEARLS 1000 - 9.0, MOGUL/BLACK PEARLS L - 4.5

REGAL 400/400R - 3.5, ALL OTHER GRADES < 2.5.

▲ ELFTEX PELLETS 115 described as "oil bound pellets" are a blend of a fluffy black and a process oil. The mixing of these components takes place after the fluffy black is produced to form a low dust easily dispersible pellet.

NOTE 1: The standard package for Cabot Special Blacks produced in the U.S. is a 3 ply kraft bag. With few exceptions, fluffy grades are packed 25 lbs. net and pelleted grades 50 lbs. net. Polyethylene overslips are available for moisture protection during storage. Polyethylene bags of 1.0 mil thickness are also available on many pelleted grades. These allow incorporation of unopened bags directly into a plastic mix. Intermediate Bulk Containers are available in 50 c.f., 60 c.f. and 84 c.f. sizes for many pelleted grades. For greater packaging details contact your local Cabot Representative.

NOTE 2: ® A registered trademark of Cabot Corporation.

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Special Blacks and their Properties

The purpose of this catalog is to help you in the selection of a suitable Special Black for your application. However, while the information contained herein serves as a general guide, we invite you to take advantage of the Special Blacks Division's technology and experience in matching a grade of black to your requirements.

Cabot Special Blacks are manufactured by a continuous process to meet rigorous specifications and satisfy end use performance requirements. It should be noted that the data included in this catalog represent typical analytical properties for purposes of grade comparison. *They do not constitute production specifications*, but rather are results of the analyses of spot production samples of these grades.

As very small differences in prime particle size distinguish many grades of carbon black, it is important to note that it is the combined effect of many properties which characterizes a particular grade's performance. The key properties are DBP oil absorption and surface area.

Carbon black is unique among commercially available pigments due to its extremely fine primary particle size (with accompanying high surface area) and very high oil (DBP) absorption. Thus, formulators are urged to exercise careful judgment in the selection of a suitable grade, and to take care in the incorporation and dispersion of the carbon black in their products. The importance of choice of a proper vehicle system and selection of an effective dispersion technique cannot be over emphasized.

The data in this brochure in no way constitute a specification or certification for any particular shipment or shipments, but simply represent values based on analyses of typical samples from production of these grades.

For further information or assistance on grade selection and dispersion, please contact your Cabot Representative or call the appropriate number listed on the back cover.

Color Index Classification:

Pigment Black #7, Constitution #77266

CAS Registry Number:

1333-86-4

HMS Rating:

0-Health 1-Flammability 0-Reactivity

National Registries:

Refer to the product Material Safety Data Sheet for further information on the hazards of carbon black and how to handle the product safely.

Surface Area:

Specific surface area is determined by Nitrogen absorption capacity using the Brunauer-Emmett-Teller procedure.

Oil (DBP) Absorption:

Essentially these data are absorption values as measured by ASTM D-2414 using Dibutylphtalate (DBP). While DBP values do provide a rough index of relative viscosity of dispersions, it is important to note that the physical and chemical properties of the carbon blacks may vary in sensitivity from system to system and result in different viscosities. The DBP absorption is a measure of carbon black structure used throughout the industry.

Particle Size:

The particle size data listed are typical arithmetic mean diameters of a sufficient number of prime particles to characterize a particular grade. Diameters are determined from Transmission Electron Microscope measurements using ASTM D-3849.

Tinting Strength:

The data reported are average values based on ASTM D-3265. A gray paste is made by mixing the carbon black with zinc oxide and a soybean oil epoxide. The reflectance of the gray paste is measured and reported as the percent strength relative to an industry reference standard.

pH:

The pH of carbon black is related to the amount of chemisorbed oxygen present on its surface. The low concentration of oxygen complexes on furnace carbon blacks and the very small amount of water soluble salts cause neutral to slightly alkaline pH values for most carbon blacks. To improve viscosity, stability and flow, several grades of carbon black (indicated with an asterisk in the table) have been surface treated to increase the amount of chemisorbed oxygen groups present. These products, therefore, have an acidic pH (2 to 4).

Bulk Density:

The values for bulk density, expressed in pounds per cubic foot, indicate the amount of space the various grades will occupy. This can be a helpful guide to required shipping and storage space and underscores one of the cost advantages of the higher density pelleted grades.

Specific Gravity:

The specific gravity of carbon black is 1.8

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Figure 2 shows a phase-contrast electron micrograph of carbon black at high resolution that displays the marked concentric arrangement of the layer planes at the surface and around what appear to be growth centers.

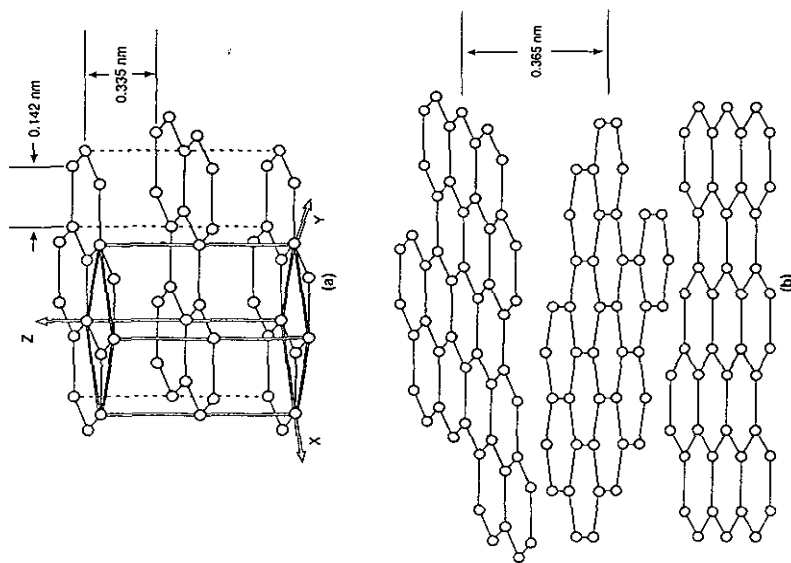


Fig. 1. Atomic structural models of (a), graphite, and (b), carbon black.

The word particle has become so widely used in the technical rubber and carbon black literature that it is convenient to retain the term when in fact nodule is meant. The layer planes are curved, distorted, and of varying size. They also intersect and interconnect one particle or nodule with its neighbors. This type of structure has been termed paracrystalline. It is obvious that individual particles do not exist in carbon blacks, with the exception of thermal blacks, and that the functional unit is an aggregate of nodules that probably existed as smaller particles at some early stage of the carbon formation process. The functional unit in well-dispersed systems is called an aggregate.

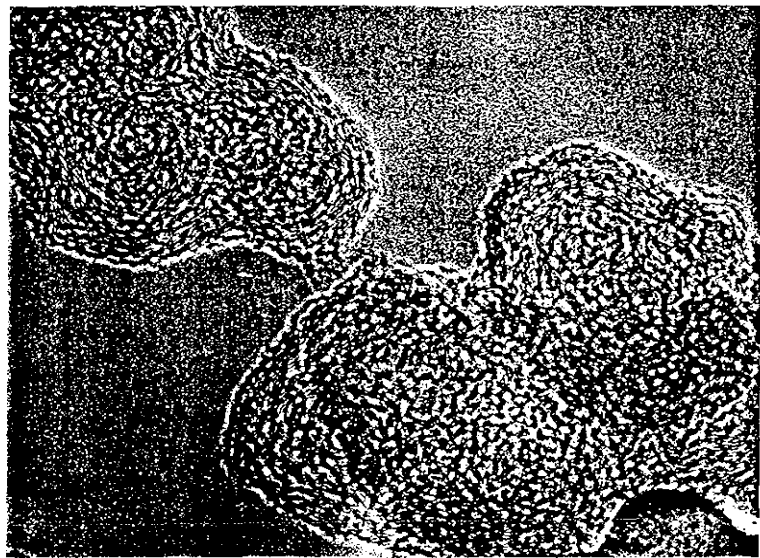


Fig. 2. High resolution (3,000,000 \times) electron micrograph of H-300-grade carbon black. Courtesy of W. M. Hess.

Morphology. In describing carbon black, three terms are used to describe structures of increasing scale and complexity:

Particles (nodules) are the primary structure element. They are roughly spherical elements that are joined in the aggregate structures.

Aggregates are the primary dispersable elements of carbon black in all but thermal blacks. The particles in an aggregate are connected and have grown together.

Agglomerates are undispersed clusters of aggregates held together by van der Waals forces or by binders. The term structure is used to describe both the extent and the complexity with which the particles are interconnected in aggregates. Primary measures of structure focus on the internal space within the aggregate.

Size and shape of the aggregates in composite systems are the principal features that determine the performance of carbon black as a reinforcing agent and as a pigment (8). Figure 3 shows an electron micrograph of a reinforcing tread black. There is an enormous range in aggregate size. The aggregate size distribution curve for N220 shown in Figure 4 is log-normal, and the range of D_e equivalent diameters of the projected areas of the aggregates is about tenfold. Within each aggregate the nodules, or particles, appear to be about the same size. The size of the aggregates is directly related to the size of the particles. The shapes of the aggregates have infinite variety from tight grape-like clusters to open dendritic or branched arrangements to fibrous configurations.

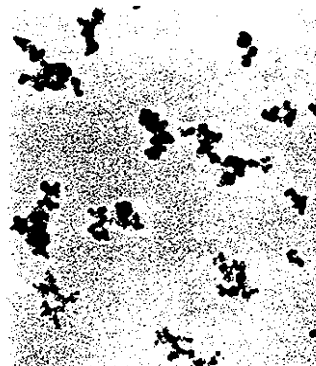


Fig. 3. Electron micrograph of reinforcing-grade of N399 tread black (100,000 \times).

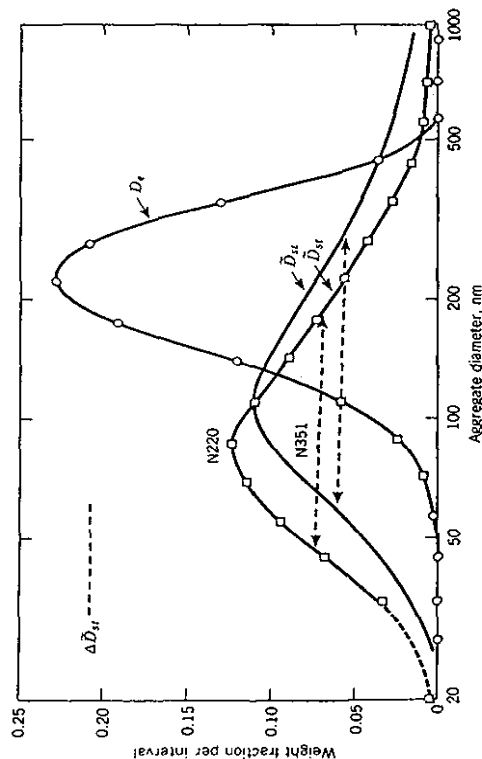


Fig. 4. Aggregate size distributions by electron microscope image analysis (D_e) and centrifugal (D_{St}) sedimentations for N220 and N351 carbon blacks (8).

A useful method for determining relative aggregate sizes and distributions is by centrifugal sedimentation. From the sedimentation rates of the aggregates the Stokes diameter is derived. A convenient instrument for these measurements is the Joyce Loebel disk photosedimentometer (9). Large aggregates sediment at a faster rate than smaller ones. The sedimentation rate is also influenced by the bulkiness of the aggregates. At constant volume or mass, a bulky aggregate sediments more slowly than a compact aggregate because of frictional drag. Figure 4 (8) shows a comparison of a Stokes diameter distribution \bar{D}_{St} and equivalent diameter distribution D_e from electron microscopy for N220. In this example the modal \bar{D}_{St} value is about one-third of the modal D_e value.

Table 1 lists average \bar{D}_{St} values from a number of literature sources. This table also lists d_{um} values for the aggregates calculated from their estimated volumes. In this case there is reasonable agreement between the two diameters. Aggregate size distributions from centrifugal sedimentation analysis are very useful for assessing the differences in this characteristic within a given grade or at constant surface area. It has been shown that the hysteresis of rubber vulcanizates can be reduced by broadening the aggregate size distribution curve without any significant loss in abrasion resistance (11,12). As shown in Figure 4 this broadening is usually expressed as ΔD_{St} , the width at 50% of the modal value. \bar{D}_{St} values have been related to the dynamic and mechanical performance of rubber-grade carbon blacks. Hysteresis decreases and abrasion loss increases with increasing values of \bar{D}_{St} (13).

Table 1. Carbon Black Morphology^a

ASTM designation	Particle size, d_{um} , nm	Aggregate size, d_{um} , nm	\bar{D}_{St} , nm	Surface area, m ² /g
N110	27	93	76-111	143
N220	32	103	95-117	117
N234	31	109	74-97	120
N326	41	108	98	94
N330	46	146	116-145	80
N339	39	122	96-125	96
N351	50	159	127	75
N375	36	106	91	105
N550	93	240	220-242	41
N660	109	252	227-283	34
N774	124	265	261	30
N990	403	593	436	9

^aRef. 10. Particle size, aggregate size, and surface area are by em.

^b d_{um} = weight mean diameter = $\frac{\sum d^4}{\sum d^3}$.

^cStokes diameter by centrifugal sedimentation from various sources.

The tinting strength of rubber-grade carbon blacks shows a linear relationship with \bar{D}_{St} shown in Figure 5. Since performance characteristics are known to

depend on aggregate volume, surface area, and bulkiness, it appears that the \bar{D}_s values combine the effects of all these factors. As such, it is a valuable addition to carbon black characterization methodology.

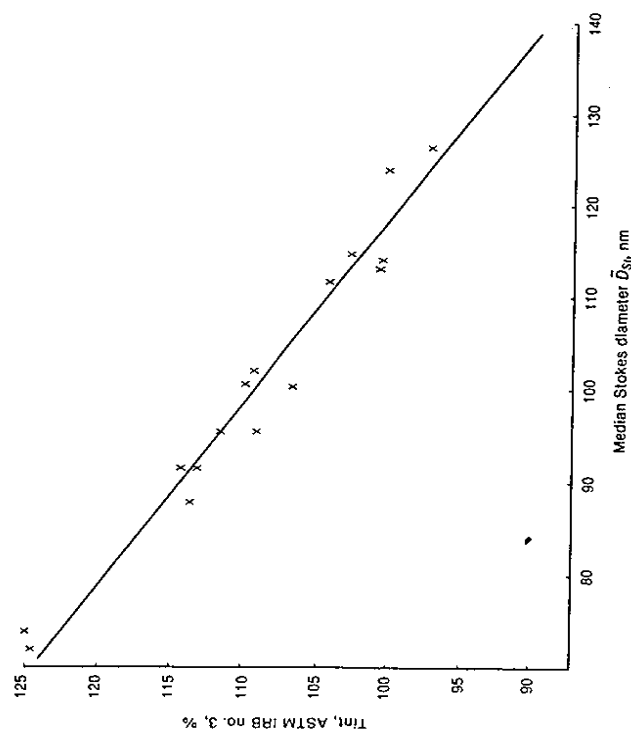


Fig. 5. Tinting strength versus median Stokes diameters for a range of reinforcing tread blacks.

Aggregate Morphology and Structure. The term structure is widely used in the carbon black and rubber industries. It was originally introduced in 1944 (14) to describe a chaining tendency of the carbon black particles. It is now used to describe the relative void volume characteristics of grades of black of the same surface area. Structure comparisons of grades with different surface areas cannot be made. It is now known that the properties associated with structure are associated principally with the bulkiness of individual aggregates. Aggregates of the same volume, surface area, and number of nodules have high structure in the open bulky and filamentous arrangement and a low structure in a more clustered compact arrangement.

High structure blacks in unvulcanized rubber give higher Mooney viscosities, lower die swell, faster extrusion rates, and better and more rapid dispersion after incorporation. In vulcanized rubber higher modulus is obtained. High structure blacks give lower bulk densities and high vehicle demand in paint systems.

Structure is usually measured by a void volume test such as the absorption

of dibutyl phthalate (DBPA) (15), or by bulk density measurements of the carbon black under compression. In order to eliminate the effects of pelletizing conditions the DBPA test has been modified to use a sample that has been pre-compressed at a pressure of 165 MPa (24,000 psi) and then broken up four successive times (24M4) (16). This procedure causes some aggregate breakdown and is claimed to more closely approximate the actual breakdown that occurs during rubber mixing.

Aggregate Breakdown. Aggregate size analysis by the electron microscope and centrifuge methods are performed on predispersed samples of carbon black. High shear energy, usually ultrasonic, and enough time are employed in these sample preparations to break down microagglomerates to their ultimate aggregates for measurement. When mixed into elastomers under high shear conditions the aggregates themselves undergo fracture forming smaller aggregates that become the actual functional units (17-19). The extent of breakdown depends on shearing stress, energy input, and the grade of carbon black. Elastomer mixes were studied using the techniques of ultramicrotome and automated image analysis. Ultrasonic dispersions of carbon gel preparations from elastomer mixes have also been used in breakdown studies. A high DBPA reinforcing tread grade (N347) exhibited a significant reduction in aggregate length in a BR/OEP tread formulation, whereas a low DBPA grade (N326) showed no measurable change. The extent of aggregate length reduction was 30 to 40% for the normal and high DBPA grades (20).

The effect of elastomer viscosity on aggregate breakdown has been shown (19). A high DBPA grade (N339) was well-mixed with a 52 and a 100 Mooney viscosity OE-SBR. A 43% reduction in aggregate volume was reported for the 52 Mooney rubber and a 53% reduction for 100 Mooney rubber. High resolution electron micrographs show actual fracture locations at the ends of aggregates. The extent of fracture from aggregate length and volume breakdown is consistent with one average fracture per aggregate for the high DBPA grades.

Chemical Composition

Oil-furnace blacks used by the rubber industry contain over 97% elemental carbon. Thermal and acetylene black consist of over 99% carbon. The ultimate analysis of rubber-grade blacks is shown in Table 2. The elements other than carbon in furnace black are hydrogen, oxygen, and sulfur, and there are mineral oxides and salts and traces of adsorbed hydrocarbons. The oxygen content is located on the surface of the aggregates as C_xO_y complexes. The hydrogen and sulfur are distributed on the surface and the interior of the aggregates. Some special blacks used for pigment purposes contain larger quantities of oxygen than normal furnace blacks. These blacks are made by oxidation in a separate process step using nitric acid, ozone, air, and other oxidizing agents. They may contain from 2 to 6% oxygen. Oxidation improves dispersion and flow characteristics in pigment vehicle systems such as lithographic inks, paints, and enamels. In rubber-grade blacks surface oxidation reduces pH and changes the kinetics of vulcanization, making the rubber compounds less scorchy and slower curing.